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<b>(54) Title:</b> MAN-MADE VITREOUS FIBRES AND THEIR PRODUCTION		
<b>(57) Abstract</b> <p>Mineral fibre products, in particular rigid bonded mineral fibre products, are provided which comprise composite mineral fibres having a coating-core configuration wherein the core provides at least 90 % by weight of the fibres and is formed of mineral melt and the coating is coated onto the core. The mineral melt is chosen so that the fibres without coating have adequate biological solubility and the coating comprises a phosphate or hydrogen phosphate of alkali metal, quaternary ammonium or ammonium in an amount of at least 0.3 % by weight of the core. The coated fibres surprisingly retain their biological solubility whilst having improved resistance to ageing in use.</p>		

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MAN-MADE VITREOUS FIBRES AND THEIR PRODUCTION

The invention relates to mineral fibre products which have a solubility in biological fluid which is considered to be acceptable but which are durable in use and are based  
5 on rock, slag, stone or other mineral melt.

Some mineral fibres are made from vitreous mineral melt, such as of rock, slag or other mineral. The melt is formed by melting in a furnace a mineral composition having the desired analysis. This composition is generally formed  
10 by blending rocks or minerals to give the desired analysis.

Although there is no scientific evidence establishing that there is a health risk associated with the manufacture and use of these mineral fibres, commercial interests have led manufacturers to provide mineral fibres that can also  
15 be alleged to be of improved biological safety.

This allegation of improved safety is usually made on the basis of in vitro test that examines the dissolution rate or degradability of the fibres in a liquid which is intended to simulate lung fluid, such as Gamble's solution  
20 at about pH 7.5. The test is normally conducted under conditions whereby the fibres are immersed in a previously prepared Gamble's solution having the specified pH.

Numerous patent applications have been published describing fibres that give enhanced dissolution rate in  
25 such an in vitro test, such as WO87/05007, WO89/12032, EP 412,878, EP 459,897, EP 558,548 WO93/22251, WO94/14717 and WO95/21799.

As is apparent from the large amount of literature, of which examples are listed above, directed to the production  
30 of fibres which have good solubility as measured by an in vitro pH 7.5 test, a large amount of research has been conducted into optimising the composition of the mineral melt (and the resultant fibres) so as to obtain this high dissolution rate. This optimisation has been applied to  
35 the production of fibres that would normally be considered as glass fibres (e.g., in EP 412878) but has especially been applied to the production of fibres which would

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normally be considered as stone, rock or slag fibres, such as in EP 459878 or EP 558548 or WO95/21799.

5 The resultant fibres meet the environmental and regulatory desire to provide fibres which, on the basis of an in vitro test, can be shown to be environmentally desirable. An unfortunate consequence is that this research may lead to the production of fibres which fail to provide one of the originally inherent advantages of mineral fibres, namely inertness to ambient humidity.

10 Thus a traditional mineral fibre product is substantially inert to the presence of atmospheric humidity whereas such a product based on cellulosic or other organic fibres may tend to collapse in the presence of atmospheric humidity.

15 Unfortunately, the mineral fibres which tend to be considered as having good biological solubility (for instance at least 20 and often at least 50nm/day) have poor resistance to atmospheric humidity, which tends to condense onto the fibres. Thus, the attainment of the allegedly desirable biological solubility is often achieved at the expense of the essential property of inertness to condensed atmospheric humidity.

20 The condensed humidity may be due to the natural humidity in the atmosphere or the humidity due to wetting of the fibre product by occasional rain or application of cement or other water, especially in enclosed constructions.

25 There have been proposals to coat stone wool fibres to improve their resistance to hydrolysis in certain environments. For instance, WO94/02427 proposes immersing rock fibres in a composition comprising silane to coat them with silane. No disclosure is given of the particular fibres which are coated, so they would be assumed to be conventional rock fibres having poor solubility in the Gamble's solution test described above. The exemplified fibres are mixed with an SBR rubber composition to form sealing rings after treatment with silane. Use as a bonded insulation product is not described.

Transferring this knowledge to fibres specifically designed to have good solubility in the Gamble's solution test would appear to defeat the purpose of conducting the research and development necessary to produce mineral fibres having good solubility in the solubility test using Gamble's solution. Accordingly, it would appear that the desire for biological solubility is incompatible with the desire for mineral fibres which are relatively unaffected by condensed ambient humidity.

Coating of fibres such as stone wool for other purposes is described for instance in JP-A-2,149,453. Fibres are treated apparently to partially melt the surface by use of a solution comprising aluminium or magnesium by phosphate and a fluoric acid.

Various coatings have also been described for other types of fibre, for instance glass fibre. EP-B-539,342 describes some of these in its background section and also describes a coating composition for glass fibres which comprises aluminium oxide, orthophosphoric acid and water, which form an anionic polymer in situ. The coating is intended to replace the organic resins often coated onto glass fibres to reduce dust and breakage during shipping and handling. WO96/27562 describes coating glass fibres to improve their mechanical strength with weak acids such as boric acid or citric acid or a fatty acid. This binder treating solution can also contain other materials which include ammonium sulphate.

DE 2,556,539 and SE 101,164 also describe glass fibres which are to be used for reinforcement of cement products. The coating is intended to protect the glass fibres from attack by the alkaline environment which prevails in cement products and various alternative coatings are given. These include inorganic acids such as silicic acid and boric acid and organic acids such as oxalic and citric acid, as well as salts of alkali metal, alkaline earth metal and ammonium which include hydrogen phosphate, hydrogen sulphate,

hydrogen carbonate, hydrogen borate, hydrogen oxalate, hydrogen citrate and hydrogen tartrate.

These disclosures relate solely to coating of glass fibres which are not designed to be soluble in the Gamble's solution test above.

The present invention is concerned with the problem of providing mineral fibres traditionally used for their properties of high insulation value and inertness, in particular in forms suitable for use where insulation properties are required. The invention is concerned with the problem of providing fibres which have satisfactory solubility in a biological environment but which do not have severely compromised resistance to atmospheric humidity when in use.

According to a first aspect of the invention we provide a mineral fibre product comprising composite man-made vitreous fibres which have a coating-core configuration wherein the core provides at least 90% by weight of the fibre and is formed of mineral melt formed from components having the following composition, expressed by weight of oxides:

	SiO <sub>2</sub>	35-60
	Al <sub>2</sub> O <sub>3</sub>	0-12
	MgO	0-30
25	CaO	10-45
	FeO (total iron)	0-15
	Na <sub>2</sub> O + K <sub>2</sub> O	0-10
	P <sub>2</sub> O <sub>5</sub>	0-10
	B <sub>2</sub> O <sub>3</sub>	0-10
30	TiO <sub>2</sub>	0-10
	Others	0-10

and chosen such that fibres formed from the core alone have a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C

and the coating is coated onto the core and comprises a salt which is a phosphate or hydrogen phosphate of

ammonium or quaternary ammonium or alkali metal in an amount of at least 0.3% based on the weight of the core.

Products of the invention containing the defined composite man-made vitreous (MMV) fibres have good ageing resistance when exposed to humidity and/or condensation despite the fact that the majority of the fibre is produced from mineral melt chosen specifically to give a fibre which would be called a "soluble" fibre without the coating. We find that it is possible to obtain fibres of this type by coating with selected phosphate-containing materials in selected amounts. We find surprisingly that the chosen coating materials give improved ageing resistance in comparison with other materials which might be expected to give equivalent performance. We find also that they do not adversely affect the biological solubility of the fibres as measured in the Gamble's solution test.

The mineral fibre products of the invention can be used for any of the purposes for which stone, rock or slag wool fibres are known. In particular they are useful in applications where the mineral fibre product is put in position and remains there over a number of months or even years, for instance insulation applications. The product may be used in bonded or unbonded form, but preferably is in bonded form.

According to a preferred second aspect of the invention we provide a rigid bonded mineral fibre product comprising composite man-made vitreous fibres having a coating-core configuration wherein the core provides at least 90% by weight of the fibre and is formed of mineral melt formed of components having the following composition, expressed by weight of oxides:

	SiO <sub>2</sub>	45-60
	Al <sub>2</sub> O <sub>3</sub>	0-4
	MgO	0-20
35	CaO	10-45
	FeO (total iron)	0-15
	Na <sub>2</sub> O + K <sub>2</sub> O	0-7

	P <sub>2</sub> O <sub>5</sub>	0-10
	B <sub>2</sub> O <sub>3</sub>	0-10
	TiO <sub>2</sub>	0-3
	P <sub>2</sub> O <sub>5</sub> + B <sub>2</sub> O <sub>3</sub>	0-10
5	Others	0-2

and chosen such that fibres formed from the core alone have a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C

and the coating is coated onto the core and comprises  
 10 a salt which is a phosphate or hydrogen phosphate of ammonium or quaternary ammonium or alkali metal in an amount of at least 0.3% based on the weight of the core.

Rigid bonded mineral fibre products have a particular need for ageing resistance but commercially they are  
 15 desired to show adequate biological solubility. By the invention we can meet both of these needs.

According to a third aspect of the invention we also provide a process for the production of a composite man-made vitreous fibre comprising providing fibres formed from  
 20 mineral melt and having the following composition, expressed by weight of oxide:

	SiO <sub>2</sub>	35-66
	Al <sub>2</sub> O <sub>3</sub>	0-12
	MgO	0-30
25	CaO	10-45
	FeO (total iron)	0-15
	Na <sub>2</sub> O + K <sub>2</sub> O	0-10
	P <sub>2</sub> O <sub>5</sub>	0-10
	B <sub>2</sub> O <sub>3</sub>	0-10
30	TiO <sub>2</sub>	0-10
	Others	0-10

the fibres having a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C,

providing a coating composition which comprises a salt  
 35 which is a phosphate or hydrogen phosphate of ammonium or quaternary ammonium or alkali metal,



and coating this coating composition onto the fibres in an amount such that the salt is present on the fibres in an amount of at least 0.3% based on the weight of fibres.

In this method we provide stone, rock or slag fibres which are designed to have good biological solubility and are termed "soluble" fibres and provide on them a coating to improve the ageing resistance of products made from these fibres. Preferably the coated fibre product of the process includes a binder. The product is cured to form a rigid bonded mineral fibre product such as traditional fire, heat or sound insulating materials, growing substrates or roof, facade or wall sheeting. It may be in the form of for instance a batt or pipe section.

In the invention the mineral melt which forms the core of the composite fibres is a rock, stone or slag melt and has a composition within the ranges set out above. Preferably the amount of MgO is 2 to 30%, the amount of CaO is 10 to 45%, the amount of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  is 0 to 10% and the amount of  $\text{B}_2\text{O}_3$  is 0 to 10%. In particular the amount of  $\text{SiO}_2$  is generally in the range 35 to 66%, often 45 to 60% and most preferably 50 to 56%. The amount of  $\text{Al}_2\text{O}_3$  is generally below 4% and preferably below 2.5%. It is usually convenient for it to be at least 0.2% and often at least 1 or 1.5%. The amount of MgO is usually below 20% and preferably below 16%, preferably below 11%. It is usually at least 4% or 6%, preferably at least 8%. The amount of CaO is generally below 35%, preferably below 30%. It is often at least 15%. The amount of FeO is generally below 12% and preferably below 8%. It can be below 3%. It may be above 2%. The amount of alkali ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) is usually below 7% and preferably below 6%. Often each is present in an amount of 0 to 2% with the total amount often being 0.1 to 3%. The total amount of  $\text{P}_2\text{O}_5 + \text{B}_2\text{O}_3$  is often in the range 3 to 10%. The amount of  $\text{TiO}_2$  is generally at least 0.1% and is usually below 2 or 3%.

In all the compositions which are used in the invention, if  $\text{Al}_2\text{O}_3$  is low, for instance below 3 or 4%,

satisfactory solubility can be achieved in the absence of  $P_2O_5$ , but it is usually preferred for the amount of  $P_2O_5$  to be at least 1 or 2%. Often it is at least 3%. Amounts of more than about 6 or 7% are usually unnecessary.  $B_2O_3$  can be included to supplement the solubility properties, in which event it is normally present in amounts of at least 1%, and usually at least 2%, although it can be present in amounts of 0 to 2%. The amount is not usually more than 6 or 7%.

The amount of other oxides is usually below 10% and preferably below 5% or 2%. Frequently it is zero. Other oxides may include  $ZrO_2$ ,  $SrO$ ,  $BaO$ ,  $ZnO$ ,  $MnO$ ,  $CuO$  and  $Cr_2O_3$ .

At least 90% by weight of the composite fibre is provided by the core which is formed from the defined mineral melt. Generally the core provides at least 95%, often at least 98%, by weight of the composite fibre. Often at least 99% or 99.5% by weight of the composite fibre is provided by the core.

The coating part of the composite fibre comprises a salt selected from ammonium, quaternary ammonium or alkali metal salts of phosphates and hydrogen phosphates. This salt is present in an amount of at least 0.3% by weight of the core. In amounts below this ageing resistance performance can be unreliable. Amounts of salt can be 0.5% and above, for instance 1 or 2% or greater, based on the weight of the core. Normally amounts of salt greater than 8% or 5% by weight of the core are not necessary. Amounts below 2% can be preferred for reasons of economy.

Ammonium salts are preferred, in particular diammonium salts. Preferred salts are diammonium hydrogen phosphate and ammonium dihydrogen phosphate.

The coating can comprise other materials. For instance it can comprise a silane. Silanes as described in WO94/02427 can be used, for instance amino silanes, alkylaminosilanes, vinyl silanes, mercaptosilanes, halogeno silanes, acrylosilanes, alkacrylosilanes, glycidyl oxy silanes, cyanosilanes, thiocyanosilanes and mixtures

thereof. Amino silanes are preferred, for instance 3-aminopropyl trimethoxysilane and 3-aminopropyl triethoxysilane. The silane may be hydrophobic.

5 When silane is included it is generally present in amounts of 0.01 to 1%, preferably 0.05 to 0.2%, based on the weight of the core. When silane and salt are combined the amount by weight of salt in the coating is usually from 0.1 to 50 times, often 2 to 30 times, the amount by weight of silane in the coating.

10 For reasons of economy and simplicity of production, products and processes may be preferred in which the coating consists essentially of one of the defined salts, or consists essentially of a mixture of two or more of the defined salts.

15 The composite fibres of the invention can be produced by the process of the third aspect of the invention. Normally fibres are produced from the mineral melt in standard fashion. These fibres are then provided with a coating by applying to them a coating composition which  
20 comprises one of the defined salts. A single coating composition may be used. Alternatively, more than one composition may be applied to the uncoated fibres. This is particularly useful if coating materials additional to the defined salt or salts are to be used, for instance silanes,  
25 or if two or more different types of salt are to be used.

Coating composition may be applied to the fibres immediately after they are formed and before they have been collected into a web, batt or other product. For instance the coating composition can be applied in the same way as  
30 binder is usually applied close to or surrounding the fibre forming apparatus, and may be applied before the binder. Coating materials may be applied as a component of binder solution applied in conventional manner.

35 Coating composition may be applied by immersing fibres or fibre mat in a solution, suspension or emulsion of coating components.

The defined salts are usually soluble and therefore usually applied in the form of an aqueous solution. If used, silanes may be soluble or insoluble in water and are usually applied in the form of a solution, emulsion or suspension in water.

Preformed fibre web may be coated if any of the components to be coated is gaseous at a convenient temperature.

Fibres may be coated in a fluid bed with the use of spray apparatus to spray a solution, dispersion, suspension or emulsion containing coating material. Fluid bed coating is particularly convenient for fibres which are used in loose fibre form rather than in web or batt form.

Water-soluble salts of the defined type, and other water-soluble salts if used, may be applied in microencapsulated form within a coating of alkali soluble material. This alkali soluble coating would dissolve when a local concentration of high pH is built up on the fibre due to condensation of ambient humidity onto the fibres. The salt or salts would then be released.

In the invention it is preferred that the coating material should be distributed across essentially the full surface area of the fibres, rather than only as spot bonds at their intersections.

Measurement of biological solubility of both the composite fibres and the core or uncoated fibres is measured by the standard test of immersion in Gamble's solution at pH 7.5 and 37°C as described by Christensen et al in Environmental Health Perspective, Volume 102, Supplement 5, October 1994, pages 83 to 86 (Stationary Set-Up).

The core or uncoated fibres have a solubility as measured by this test of at least 20 nm/day, preferably at least 40 or 50 nm/day and often 60 nm/day or greater. Solubility may be up to 100 nm/day.

Preferably the composite coated fibres also have adequate biological solubility and therefore preferably

they also give solubility of at least 20 nm/day using this test, preferably at least 40 or 50 nm/day and often 60 nm/day or greater. Solubility may be up to 100 nm/day.

5 The invention provides composite fibres which have good ageing resistance, that is to say they have good resistance to condensation and ambient humidity. Ageing resistance may be measured in various different ways. Three accelerated ageing tests which we find useful are as follows.

10 The first method (the "first immersion test") comprises immersing 300 mg coated or uncoated fibres in 15 ml deionised water initially at pH 7.5 and 37°C. This test is designed to simulate the effect of small amounts of condensation on the fibres.

15 This test may also be carried out at various other temperatures to simulate different potential environments. In general we believe that higher temperatures of exposure result in greater dissolution rate.

20 The second method (the "second immersion test") comprises immersing 0.5g of fibres in 10ml deionised water initially at pH 7.5 in a polyethylene flask with lid for the specified amount of time and at specified temperature.

25 The third method is the "condensation test". In this method fibres are exposed to 100% relative humidity at 70°C in a climate cupboard. In this third test also various temperatures can be used.

30 Assessment of dissolution under these ageing tests can be carried out in various ways. We have found that the most reliable method is measurement of the pH surrounding the fibres. A high or generally increasing pH, in particular above pH 11, indicates degradation of the fibres. Where the pH can be caused to decrease over time or to remain at a steady, low value, in particular below pH 11, for instance below pH 10.5, this indicates good ageing resistance.

35 Other methods of assessing dissolution can be used. For instance the levels of salts in the dissolution water

can be measured, to assess how much of the fibre material has dissolved into the water. Measurements can be used which are similar to those used for the Gamble's solution test, giving results in nm/day. Microscopy, for instance  
5 scanning electron microscopy (SEM), can also be used. We find these methods useful in combination with pH measurement, but used alone they can be less reliable statistically than the pH measurement tests.

The invention will now be illustrated with reference  
10 to the following examples.

Example 1

Fibres were produced having the following composition:

	SiO <sub>2</sub>	47.6%
	Al <sub>2</sub> O <sub>3</sub>	1.5%
15	TiO <sub>2</sub>	less than 0.1%
	FeO (total iron)	0.6%
	CaO	37.1%
	MgO	11.1%
	Na <sub>2</sub> O	less than 0.1%
20	K <sub>2</sub> O	0.2%.

All percentages are by weight based on the oxide.

Coating of the fibres is carried out as follows:

3g of fibres plus 50g coating solution is placed in an ultrasound bath for 10 minutes. Surplus liquid is drained  
25 off. The fibres are dried in a rotary film evaporator at water pump vacuum at 60°C and cured at 200°C for 15 minutes.

Exposure and accelerated ageing under simulated in-use conditions is carried out as follows:

30 0.5g of fibres (coated or uncoated) are immersed in 10 ml deionised water in a polyethylene flask with lid for the specified amount of time and at the specified temperature (e.g. 70°C). Similar results could be achieved using 300 mg fibres and 15 ml deionised water.

35 The tests carried out are as follows in Table 1 below.

Table 1

Test	Coating (% by weight on fibres)		Exposure Temperature (°C)	Exposure Time (days)
	Silane	Salt		
(i)	-	1% DAHP	70	28
(ii)	0.1%	2% DAHP	70	21

The coating amounts are given as percentage of total uncoated fibre weight. Each component is present in the coating solution in an amount of one tenth the amount based on fibre weight. The silane used is 3-amino propyl-triethoxy silane. The salt used is diammonium hydrogen phosphate (DAHP).

After the exposure tests observation of the coated and uncoated fibres shows that the coating has imparted some protection against erosion in the presence of humidity.

We find that protection can sometimes be obtained with the use of diammonium sulphate (eg at 5% or 10%, with or without 0.1% silane) as a coating material instead of phosphate, but this can be unreliable and is effective only in these larger, less economic amounts. The use of the silane alone (eg at 1%) tends not to give good results at low concentrations.

#### Example 2

Fibres were produced having the following composition:

20	SiO <sub>2</sub>	47.6%
	Al <sub>2</sub> O <sub>3</sub>	1.5%
	TiO <sub>2</sub>	less than 0.1%
	FeO (total iron)	0.6%
	CaO	37.1%
25	MgO	11.1%
	Na <sub>2</sub> O	less than 0.1%
	K <sub>2</sub> O	0.2%

All percentages are by weight based on the oxide.

Coating of the fibres is carried out as described in Example 1.

The test simulating in-use conditions was carried out as described in Example 1 at a temperature of 70°C.

Coating compositions are given below. All percentages are by weight based on the weight of the uncoated fibres. The silane used was 3-aminopropyl-triethoxy silane.

Ageing resistance was assessed by measuring the pH in the solution surrounding the fibres after various periods



of time. Results are shown in the graphs attached as Figures 1 to 10.

The compositions used are as follows:

- |    |    |  |
|----|----|--|
|    | 1A | 0.01% silane   |
| 5  | 1B | 0.01% silane + 0.1% DAHP                                 |
|    | 1C | 0.01% silane + 0.2% DAHP                                 |
|    | 1D | 0.01% silane + 0.5% DAHP                                 |
|    | 1E | 0.01% silane + 1% DAHP                                   |
|    | 1F | 0.01% silane + 2% DAHP                                   |
| 10 | 1G | uncoated   |
|    |    |  |
|    | 2A | 0.1% silane  |
|    | 2B | 0.1% silane + 0.1% DAHP                                  |
|    | 2C | 0.1% silane + 0.5% DAHP                                  |
| 15 | 2D | 0.1% silane + 1% DAHP                                    |
|    | 2E | uncoated   |
|    |    |  |
|    | 3A | 0.5% silane  |
|    | 3B | 0.5% silane + 0.1% DAHP                                  |
| 20 | 3C | 0.5% silane + 0.5% DAHP                                  |
|    | 3D | 0.5% silane + 1% DAHP                                    |
|    | 3E | uncoated   |
|    |    |  |
|    | 4A | 0.1% silane  |
| 25 | 4B | 0.1% silane + 0.1% diammonium sulphate (DAS)             |
|    | 4C | 0.1% silane + 0.5% DAS                                   |
|    | 4D | 0.1% silane + 1% DAS                                     |
|    | 4E | uncoated   |
|    |    |  |
| 30 | 5A | 0.1% silane  |
|    | 5B | 0.1% silane + 0.1% aluminium ammonium sulphate (AAS)     |
|    | 5C | 0.1% silane + 0.5% AAS                                   |
|    | 5D | uncoated   |
|    |    |  |
| 35 | 6A | 0.01% silane   |
|    | 6B | 0.01% silane + 0.1% ammonium dihydrogen phosphate (ADHP) |

	6C	0.01% silane + 1% ADHP
	6D	uncoated
	7A	0.5% silane
5	7B	0.5% silane + 0.1% ADHP
	7C	0.5% silane + 1% ADHP
	7D	uncoated
	8A	0.1% silane
10	8B	0.1% silane + 0.1% ADHP
	8C	0.1% silane + 0.2% ADHP
	8D	0.1% silane + 0.5% ADHP
	8E	0.1% silane + 1% ADHP
	8F	uncoated
15	9A	0.1% DAHP
	9B	0.5% DAHP
	9C	1% DAHP
	9D	2% DAHP
20	9E	uncoated
	10A	0.1% ADHP
	10B	0.5% ADHP
	10C	1% ADHP
25	10D	2% ADHP
	10E	uncoated
	11A	1% DAS
	11B	uncoated.
30		

The results shown in the attached tables show the consistent maintenance of a lowered pH when 0.3% or more of DAHP or ADHP is included in the coating. This improvement is observed with and without silane.

35 The results in Figures 4, 5 and 11 show that sulphates give inconsistent and unreliable results, in contrast with

the reliable stabilisation obtained using amounts of DAHP and ADHP as low as 0.3%.

5       Some of the above results were confirmed by taking SEM photographs of the fibres before and after four weeks exposure in this test. Other coatings were also used. The table below indicates ("yes" or "no") whether or not the fibres underwent significant erosion during the four-week test period.

	Composition	Erosion
	1A	YES
	1B	YES
5	1C	NO
	1D	NO
	1E	NO
	1F	NO
	2A	YES
10	2B	NO
	2C	NO
	2D	NO
	3A	YES
	3B	YES
15	3C	NO
	3D	NO
	4B	YES
	4C	YES
	4D	NO
20	5B	YES
	5C	YES
	6B	NO
	6C	NO
	7B	YES
	7C	NO
25	8B	YES
	8D	NO
	8E	NO
	9A	YES
30	9B	NO
	9C	NO
	9D	NO
	10A	YES
	10B	NO
	10C	NO
35	11A	YES
	0.01% silane + 0.1% AAS	YES
	5% silane	NO
	Ion exchanged water	YES
40	Uncoated	YES

The solubility of the fibres in the Gamble's solution test was also measured. The coated fibres remain substantially similar in biological solubility to the uncoated fibres.

5 Comparative Example

Fibres were produced having the same composition as in Example 1.

Coating of the fibres is carried out as described in Example 1.

10 The test simulating in-use conditions was carried out as described in Example 1 at a temperature of 70°C.

As coating was used oxalic acid in an amount of 1% of the fibre weight.

15 After the exposure tests observations of the coated and uncoated fibres shows that the coating did not impart protection against corrosion in the presence of humidity.

CLAIMS

1. A mineral fibre product comprising composite man-made vitreous fibres which have a coating-core configuration wherein the core provides at least 90% by weight of the fibre and is formed of mineral melt formed from components having the following composition, expressed by weight of oxides:

	SiO <sub>2</sub>	35-66
	Al <sub>2</sub> O <sub>3</sub>	0-12
10	MgO	0-30
	CaO	10-45
	FeO (total iron)	0-15
	Na <sub>2</sub> O + K <sub>2</sub> O	0-10
	P <sub>2</sub> O <sub>5</sub>	0-10
15	B <sub>2</sub> O <sub>3</sub>	0-10
	TiO <sub>2</sub>	0-10
	Others	0-10

and chosen such that fibres formed from the core alone have a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C

and the coating is coated onto the core and comprises a salt which is a phosphate or hydrogen phosphate of ammonium or quaternary ammonium or alkali metal in an amount of at least 0.3% based on the weight of the core.

2. A product according to claim 1 in which the salt is an ammonium salt.

3. A product according to claim 1 or claim 2 in which the salt is diammonium hydrogen phosphate or ammonium dihydrogen phosphate.

4. A product according to any preceding claim in which the mineral melt is formed from components such that fibres formed from the core alone have a solubility of at least 40 nm/day in Gamble's solution at pH 7.5 and 37°C.

5. A product according to any preceding claim which has a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C.

6. A product according to any preceding claim in which the coating additionally comprises a silane.

7. A product according to claim 6 in which the amount of silane in the coating is from 0.01 to 1% based on the weight of the core and the salt is a salt of ammonium or alkali metal and is preferably present in an amount of at least 1% based on the weight of the core.

8. A product according to any preceding claim in which the mineral melt is formed from components having the following composition, expressed by weight of oxides:

	SiO <sub>2</sub>	45-60
	Al <sub>2</sub> O <sub>3</sub>	0.2-4
	MgO	6-16
	CaO	10-45
15	FeO	2-15
	Na <sub>2</sub> O+K <sub>2</sub> O	0-7
	P <sub>2</sub> O <sub>5</sub>	0-5
	B <sub>2</sub> O <sub>3</sub>	0-2
	TiO <sub>2</sub>	0-3
20	Others	0-2

9. A product according to any preceding claim in which the amount of salt is not more than 2%, preferably not more than 1%, based on the weight of the core.

10. A product according to any preceding claim which is a rigid bonded mineral fibre product.

11. A product according to claim 10 which is a batt or pipe section.

12. A product according to claim 10 which is a growing substrate.

13. A product according to any of claims 10 to 12 in which the mineral melt is formed from components having the following composition, expressed by weight of oxides:

	SiO <sub>2</sub>	45-60
	Al <sub>2</sub> O <sub>3</sub>	0-4
35	MgO	0-20
	CaO	10-45
	FeO	0-15

	$\text{Na}_2\text{O}+\text{K}_2\text{O}$	0-7
	$\text{P}_2\text{O}_5$	0-10
	$\text{B}_2\text{O}_3$	0-10
	$\text{TiO}_2$	0-3
5	$\text{P}_2\text{O}_5+\text{B}_2\text{O}_3$	0-10
	Others	0-10

14. A process for the production of a composite man-made vitreous fibre comprising providing fibres formed from mineral melt and having the following composition, expressed by weight of oxide:

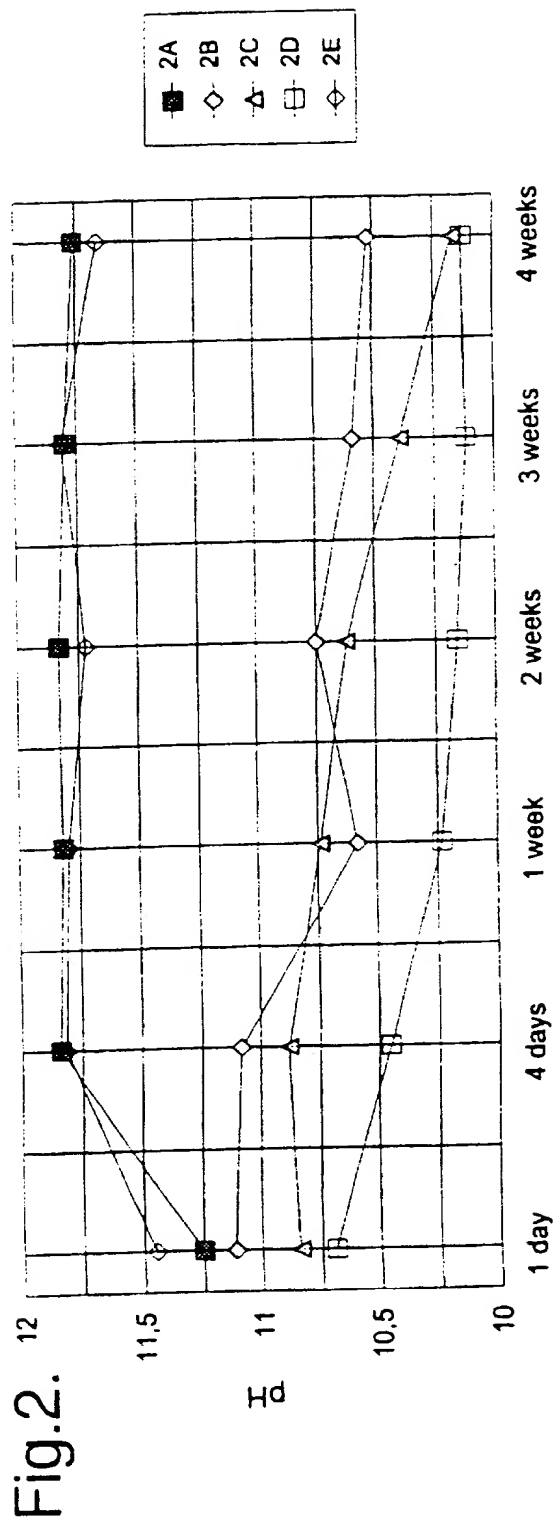
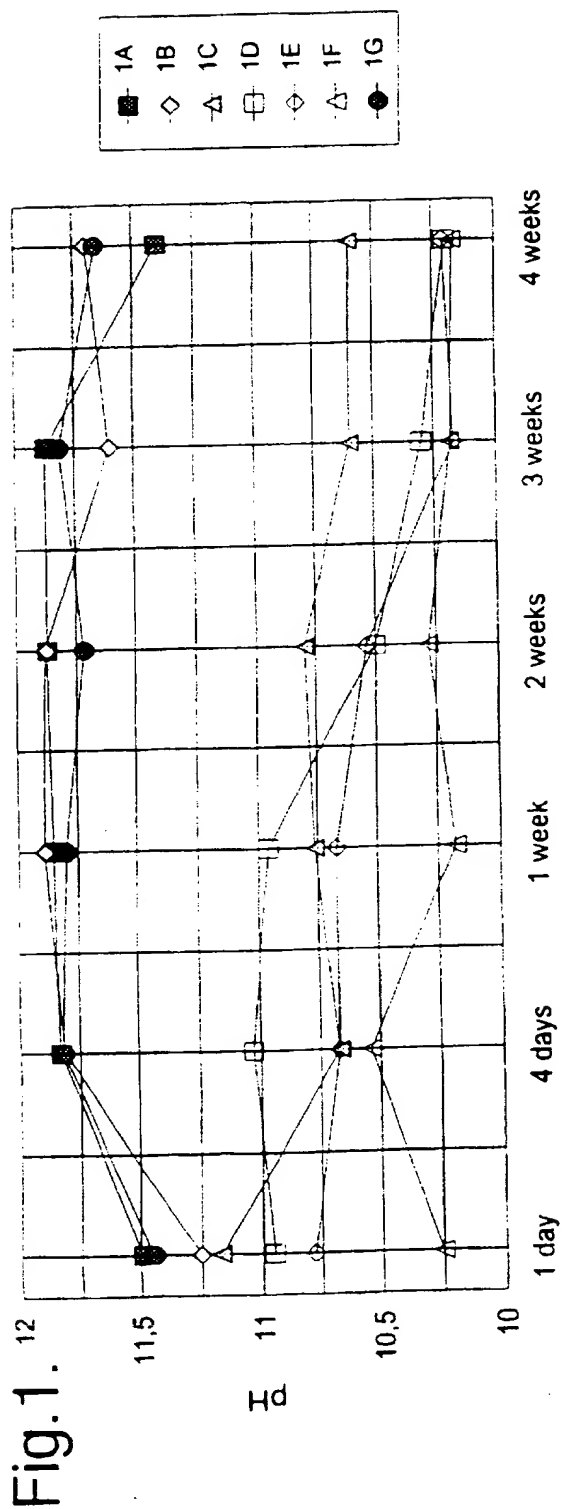
10	$\text{SiO}_2$	35-66
	$\text{Al}_2\text{O}_3$	0-12
	$\text{MgO}$	0-30
	$\text{CaO}$	10-45
15	$\text{FeO}$ (total iron)	0-15
	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0-10
	$\text{P}_2\text{O}_5$	0-10
	$\text{B}_2\text{O}_3$	0-10
	$\text{TiO}_2$	0-10
20	Others	0-10

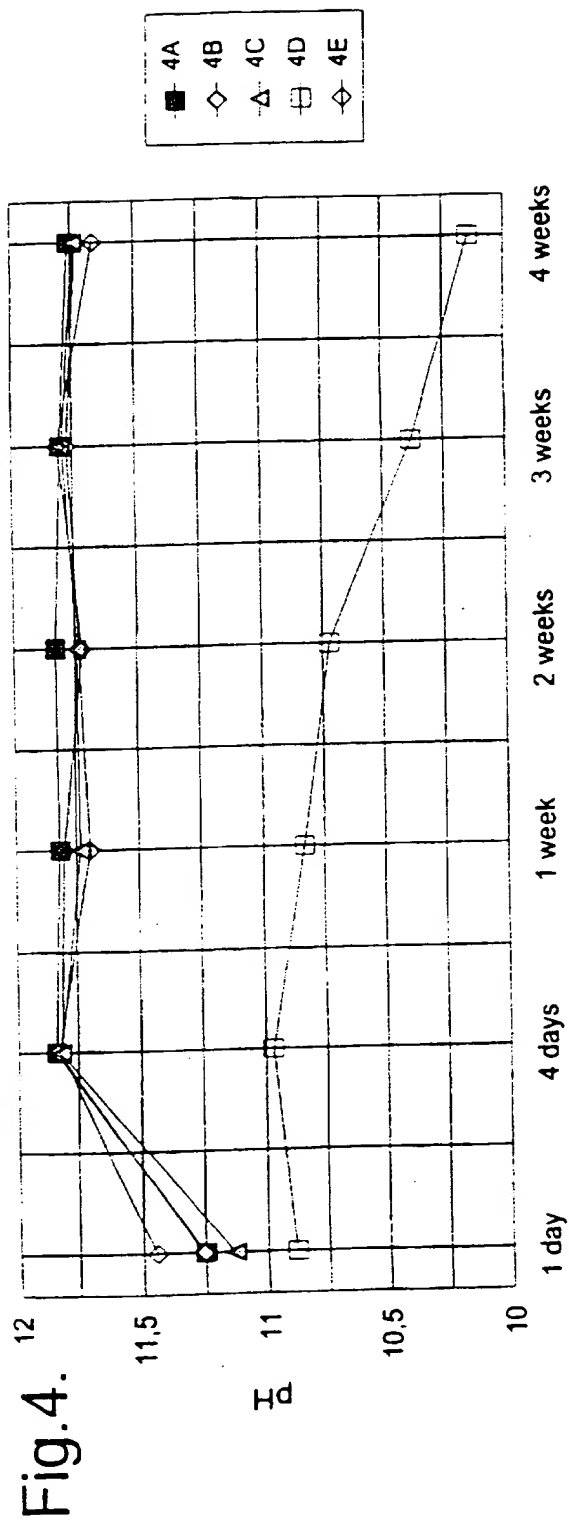
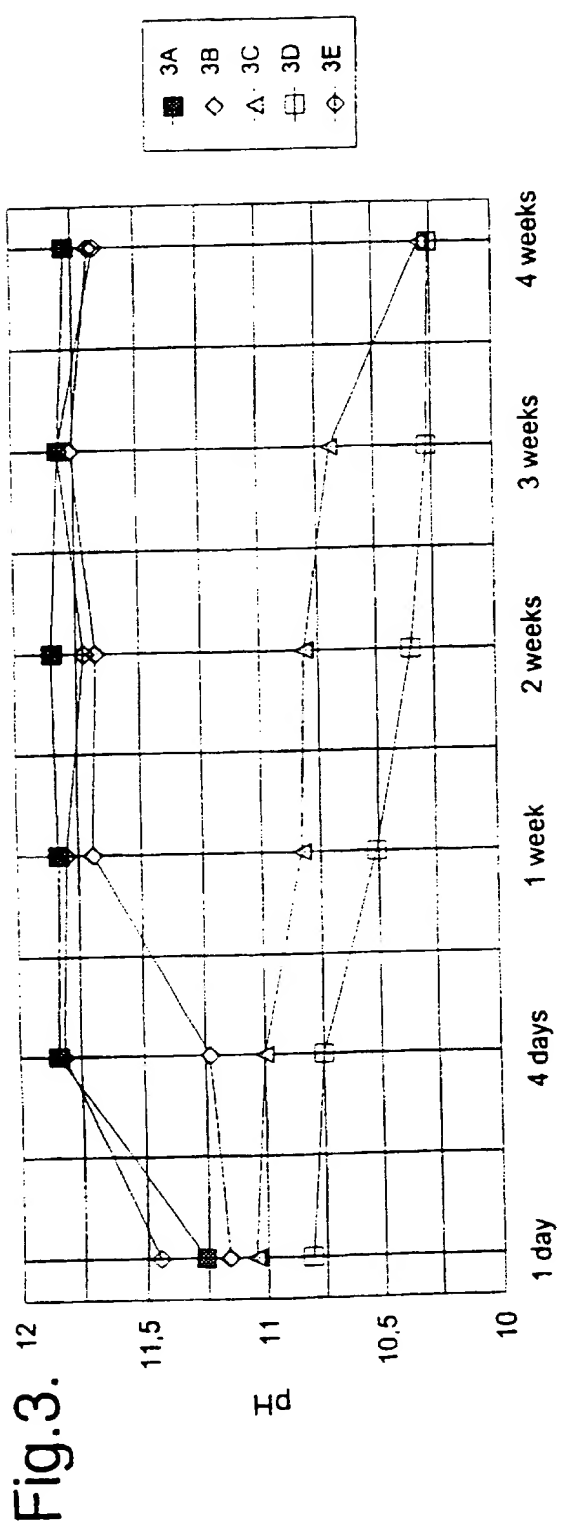
the fibres having a solubility of at least 20 nm/day in Gamble's solution at pH 7.5 and 37°C,

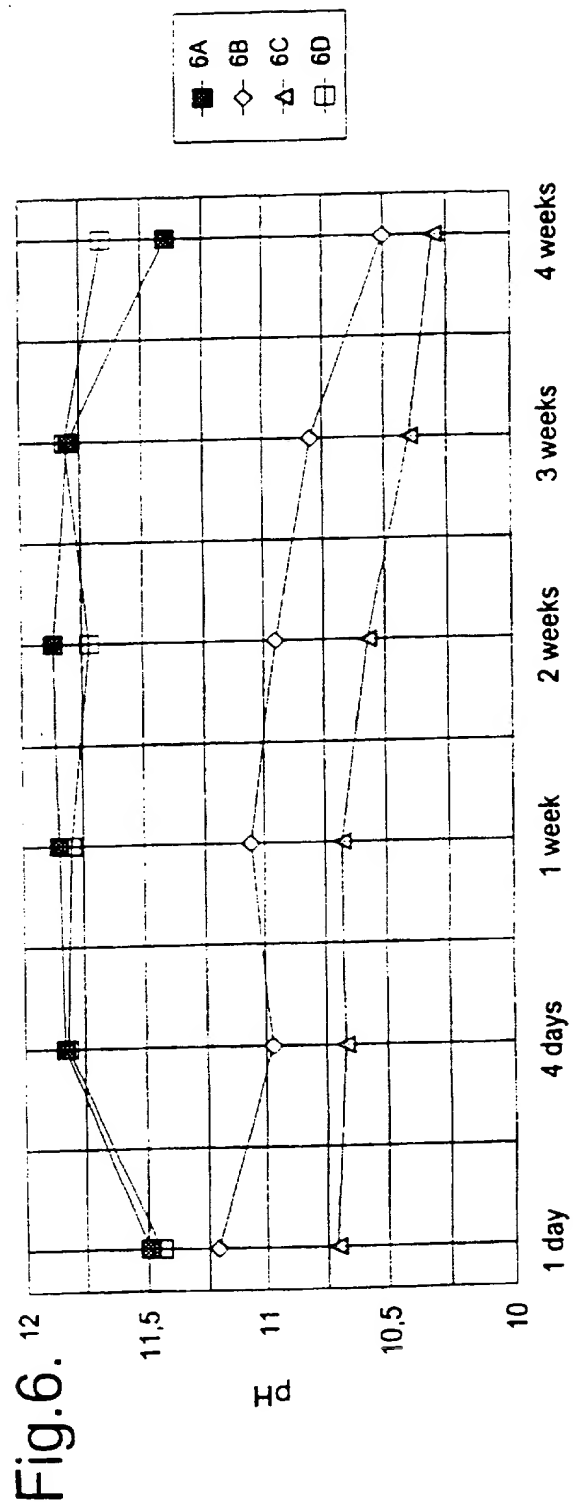
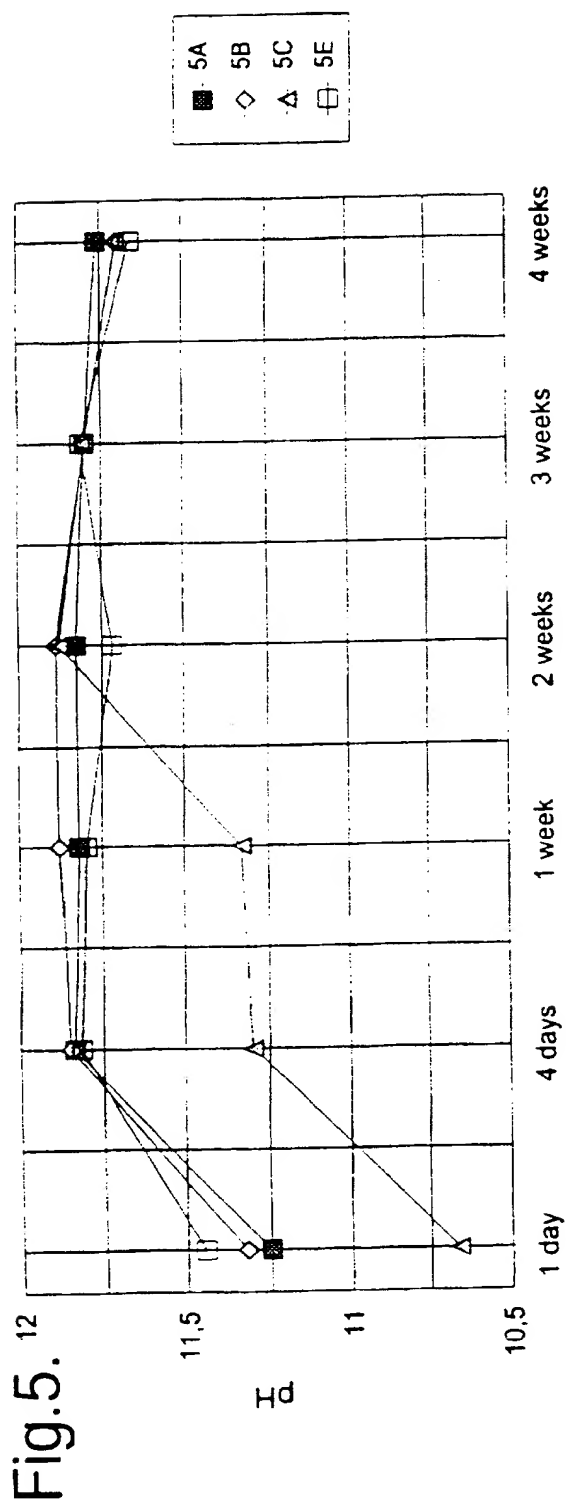
providing a coating composition which comprises a salt which is a phosphate or hydrogen phosphate of ammonium, quaternary ammonium or alkali metal,

and coating this coating composition onto the fibres in an amount such that the salt is present on the fibres in an amount of at least 0.3% based on the weight of fibres.

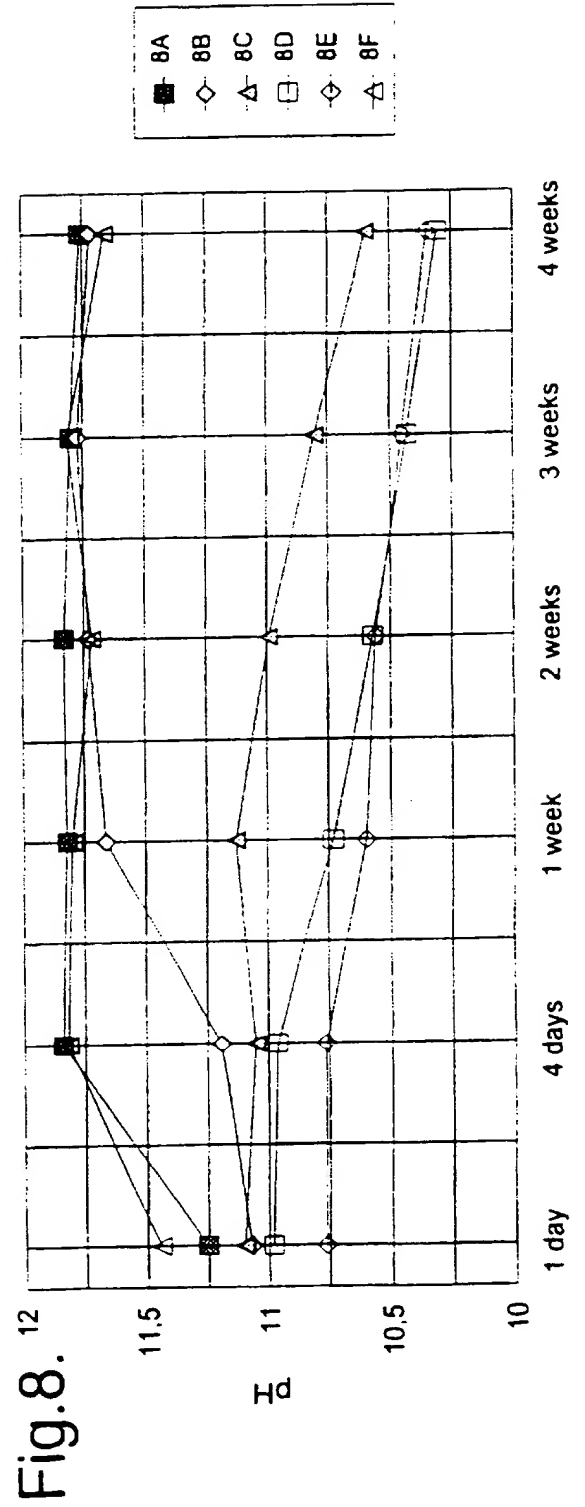
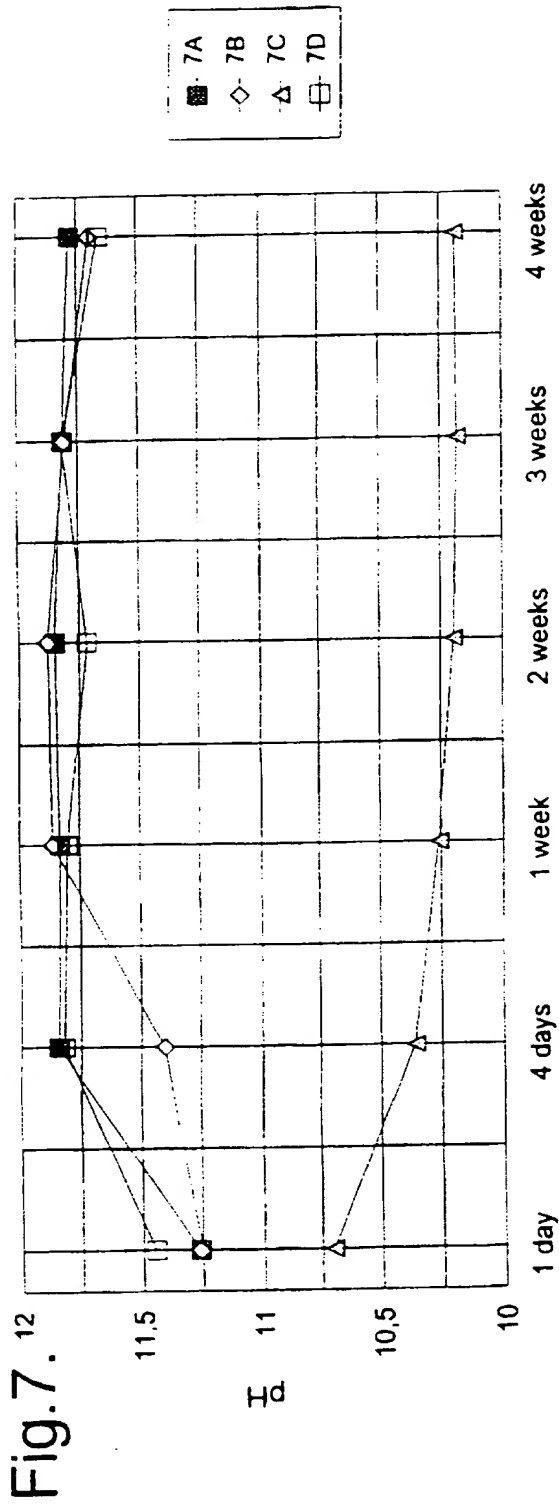




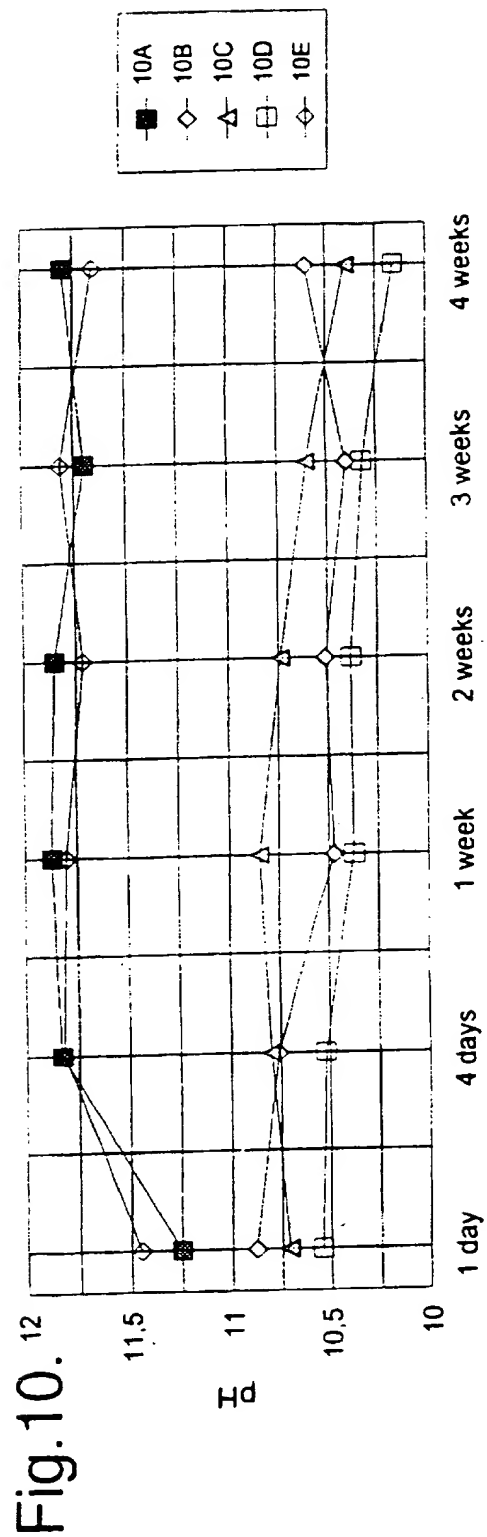
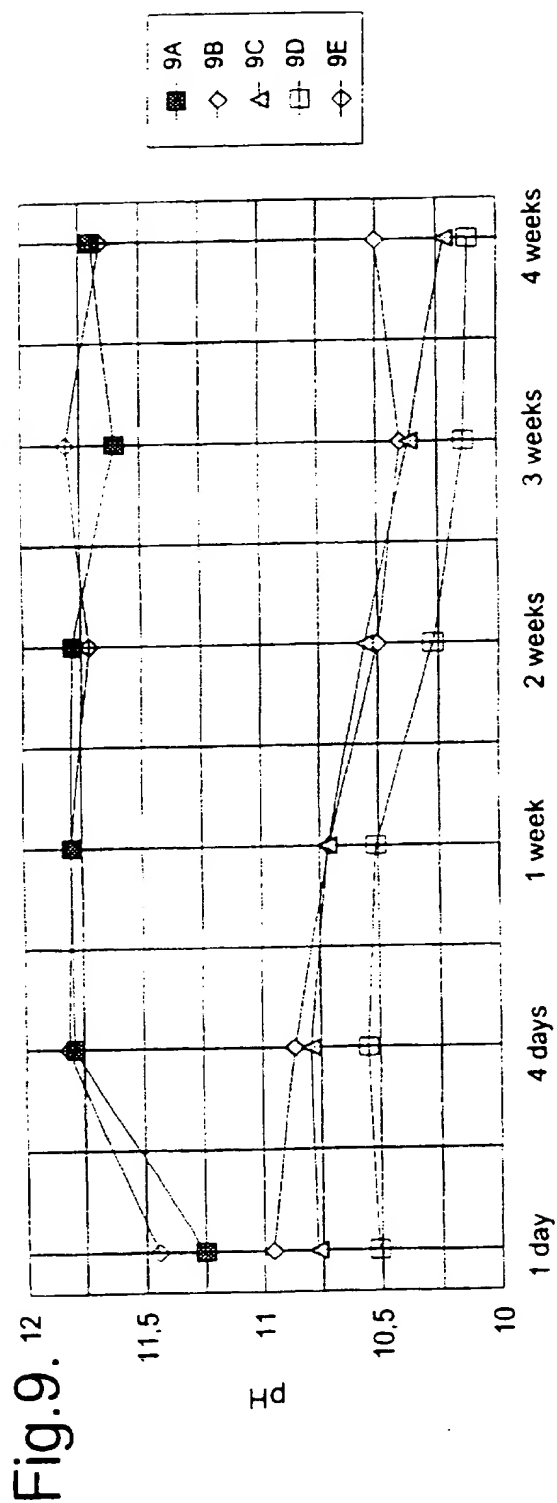




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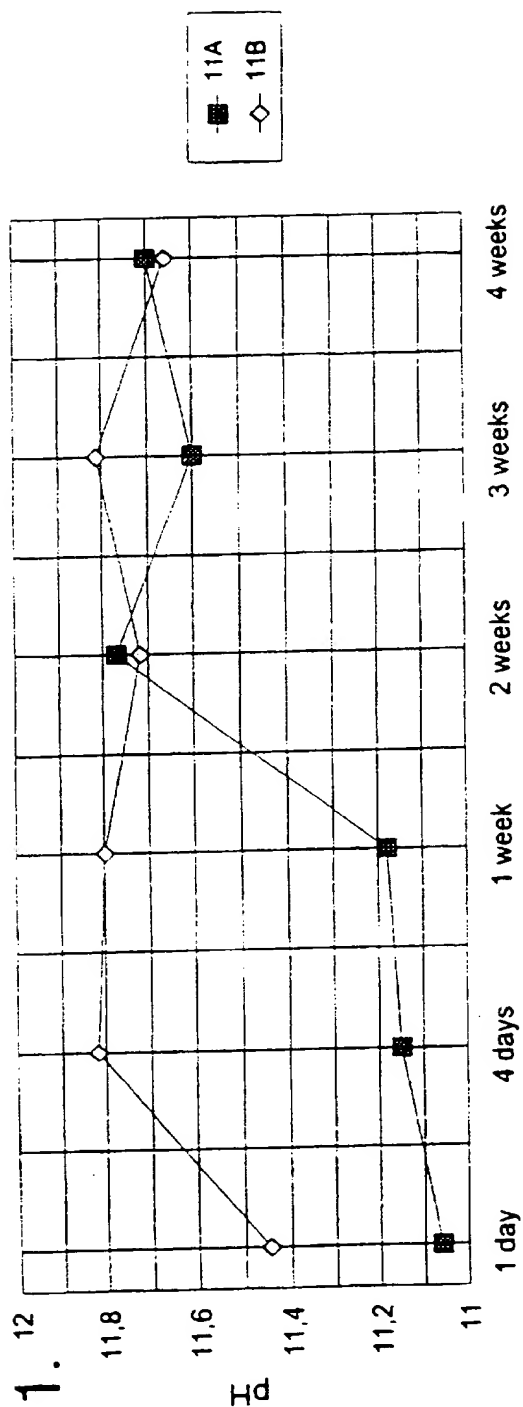


Fig. 11.

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 96/05617

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C25/02

According to International Patent Classification (IPC) or to both national classification and IPC:

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 473 392 A (JAPAN INORGANIC MATERIAL) 11 May 1977 see page 1, line 1 - page 2, line 51 ---	1-14
A	US T979008 I (PEZZOLI P A) 6 February 1979 see abstract ---	1-14
A	WO 95 29135 A (ROCKWOOL INT ; JENSEN SOREN LUND (DK); CHRISTENSEN VERMUND RUST (DK) 2 November 1995 see page 3, line 32 - page 7, line 26 -----	1-14

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

2 April 1997

Date of mailing of the international search report

09.04.97

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# INTERNATIONAL SEARCH REPORT

Inter nal Application No

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Patent document  
cited in search report

Publication  
date

Patent family  
member(s)

Publication  
date

WO 9529135 A

SK 157395 A

08-05-96



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 96/05617

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1473392 A	11-05-77	JP 50097628 A	02-08-75
		JP 50095596 A	30-07-75
		JP 50121599 A	23-09-75
		JP 1134095 C	14-02-83
		JP 50077692 A	25-06-75
		JP 57022902 B	15-05-82
		JP 1165865 C	08-09-83
		JP 50077693 A	25-06-75
		JP 57055664 B	25-11-82
		JP 1165866 C	08-09-83
		JP 50077694 A	25-06-75
		JP 57055665 B	25-11-82
		JP 1134096 C	14-02-83
		JP 50077695 A	25-06-75
		JP 57022903 B	15-05-82
		JP 1165867 C	08-09-83
		JP 50077696 A	25-06-75
		JP 57055666 B	25-11-82
		JP 1186194 C	20-01-84
		JP 50090797 A	21-07-75
		JP 58015450 B	25-03-83
		JP 1186195 C	20-01-84
		JP 50090798 A	21-07-75
		JP 58015451 B	25-03-83
		AU 6761974 A	09-10-75
		CA 1036436 A	15-08-78
		GB 1473391 A	11-05-77
		US 4017322 A	12-04-77
-----			
US T979008 I	06-02-79	NONE	
-----			
WO 9529135 A	02-11-95	AU 2446395 A	16-11-95
		AU 6679594 A	08-11-94
		CA 2165081 A	02-11-95
		CZ 9503297 A	12-06-96
		EP 0695206 A	07-02-96
		EP 0703879 A	03-04-96
		FI 955973 A	13-12-95
		PL 312244 A	01-04-96
		SI 9520005 A	31-08-96

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